

(12) **UK Patent Application** (19) **GB** (11) **2 238 486** (13) **A**
(43) Date of A publication 05.06.1991

(21) Application No **9024566.3**

(22) Date of filing **12.11.1990**

(30) Priority data
(31) **01292278** (32) **13.11.1989** (33) **JP**

(71) Applicants
Hitachi, Ltd

(Incorporated in Japan)

**6 Kanda Surugadal 4-chome, Chiyoda-ku, Tokyo,
Japan**

Babcock-Hitachi Kabushiki Kaisha

(Incorporated in Japan)

6-2 2-chome, Ohtemachi, Chiyoda-ku, Tokyo, Japan

(72) Inventors
**Noriko Watanabe
Hisao Yamashita
Akira Kato**

(51) INT CL^s
B01J 23/68, B01D 52/36

(52) UK CL (Edition K)
**B1E EAA E1161 E1191 E1206 E1208 E1213 E1298
E1315 E1332 E1342 E1441 E1461 E1462 E1492
E1497 E1513 E1611 E1621 E1622 E1626 E1631
E1634 E1635 E1701 E1702 E1708 E1709 E1714
E1721 E1738 E1741 E1743**

(56) Documents cited
**GB 1565000 A GB 1401871 A GB 0667680 A
EP 0361385 A**

(58) Field of search
**UK CL (Edition K) B1E
INT CL^s A61L, B01D, B01J
Online: WPI AND CLAIMS**

**Nobuo Matsuo
Hiroshi Akama**

(74) Agent and/or Address for Service
**Mewburn Ellis
2 Cursitor Street, London EC4A 1BQ, United Kingdom**

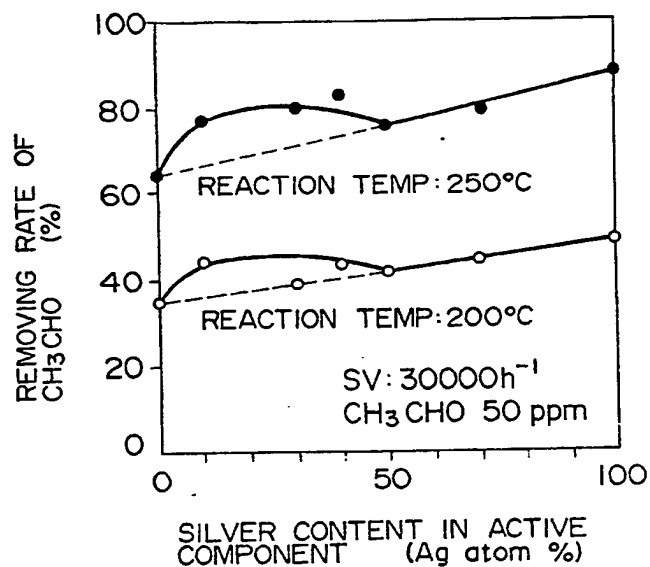
(54) **Catalyst for oxidation or decomposition of gas containing odor components**

(57) A catalyst for oxidation or decomposition of a gas containing odor components at a temperature of from room temperature to 300°C in the presence of oxygen to make the gas harmless comprises a carrier and an active component supported on the carrier and contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50.

The silver and manganese are in the form of their oxides or a silver, manganese and oxide complex.
Specific compounds destroyed by the catalyst in examples are acetaldehyde, methyl mercaptan and trimethylamine.

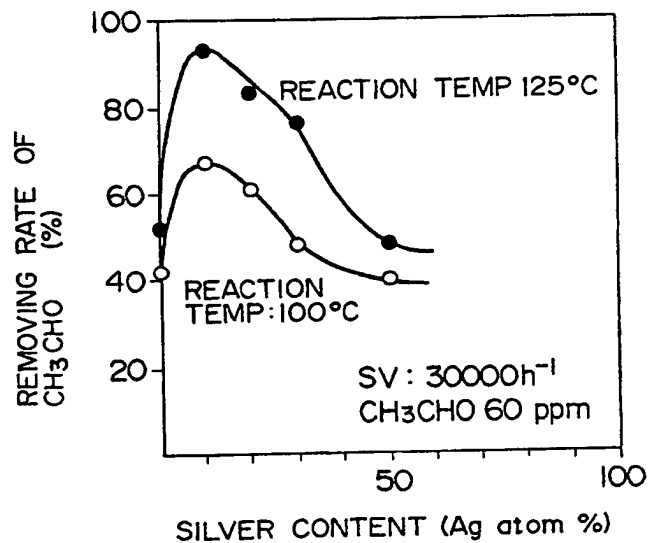
GB 2 238 486 A

FIG. 1



SILVER CONTENT AND CH_3CHO
REMOVING ACTIVITY OF Ag/Mn
CATALYST SUPPORTED ON $\gamma\text{-Al}_2\text{O}_3$

FIG. 2



DEPENDENCE OF ACTIVITY OF
Ag/Mn BULK CATALYST ON SILVER
CONTENT

7/2

FIG. 3
(COMP. EX. 1)

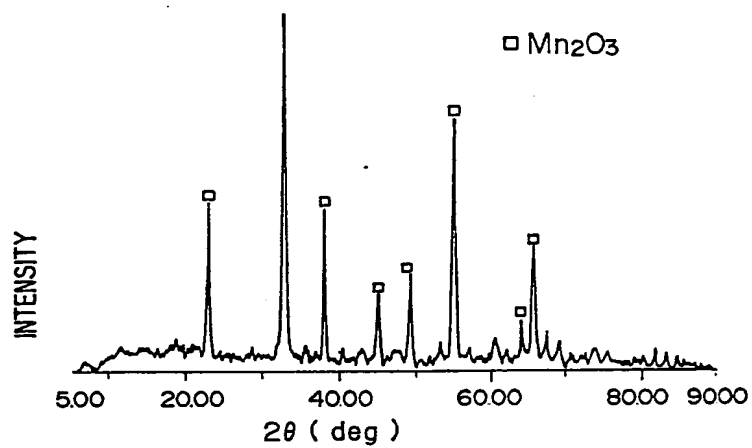


FIG. 4
(COMP. EX. 2)

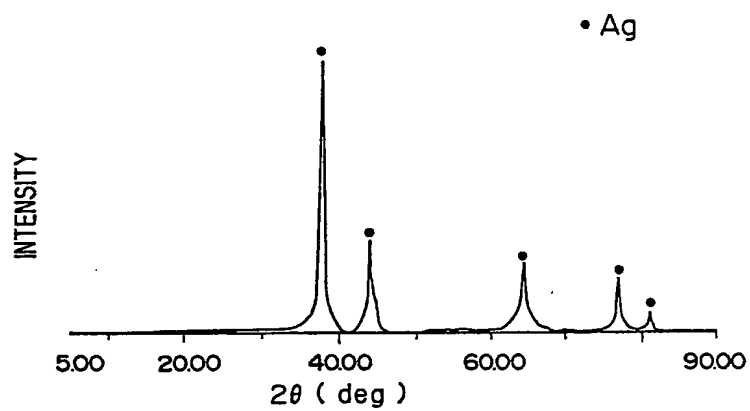


FIG. 5
(COMP. EX. 3)

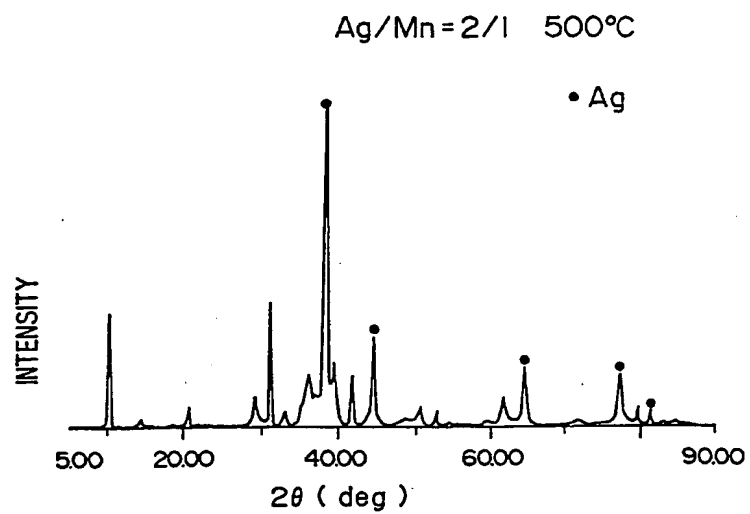


FIG. 6
(EX. 2)

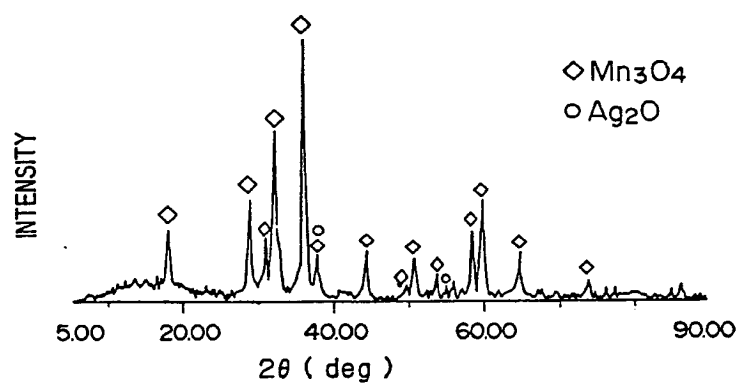


FIG. 7
(EX. 4)

$\text{Ag}/\text{Mn} = 3/7$ 500°C

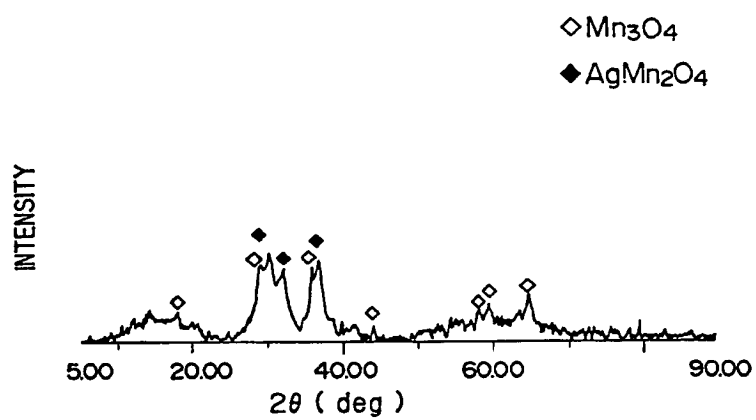


FIG. 8

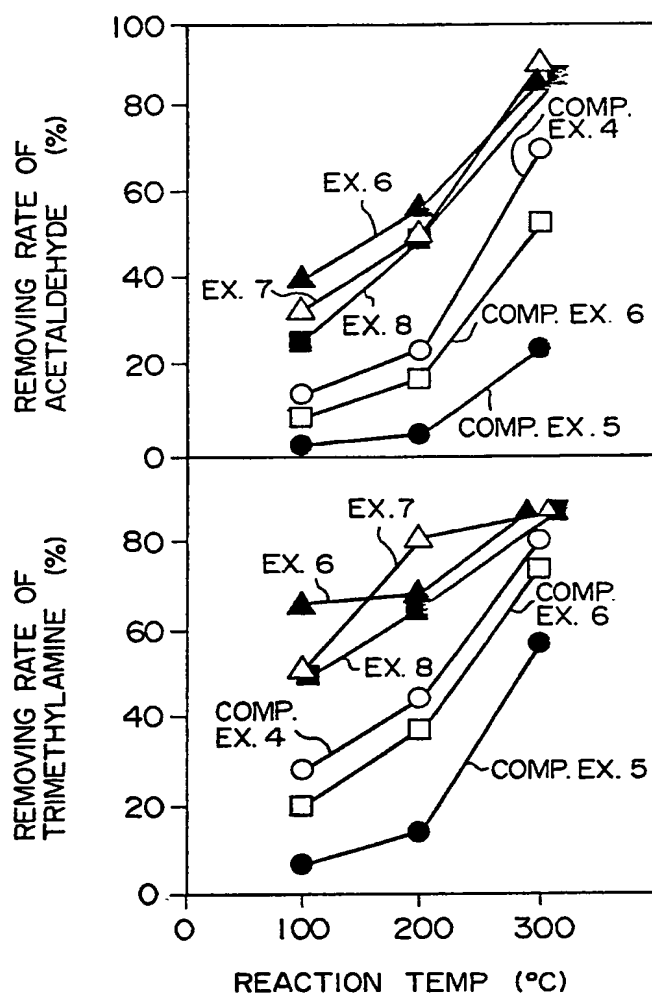


FIG. 9

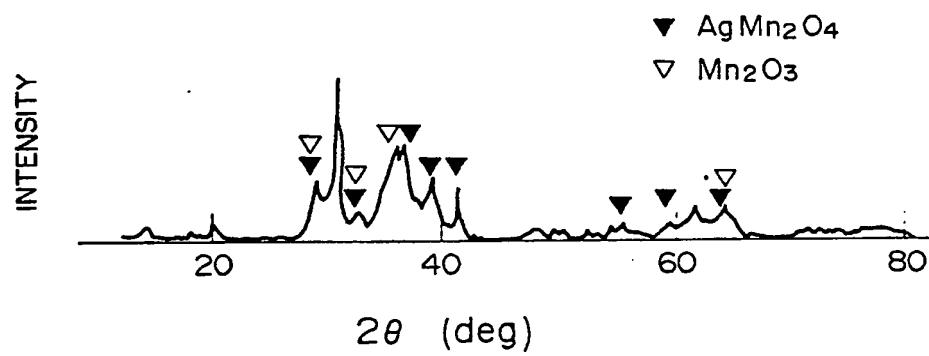


FIG. 10

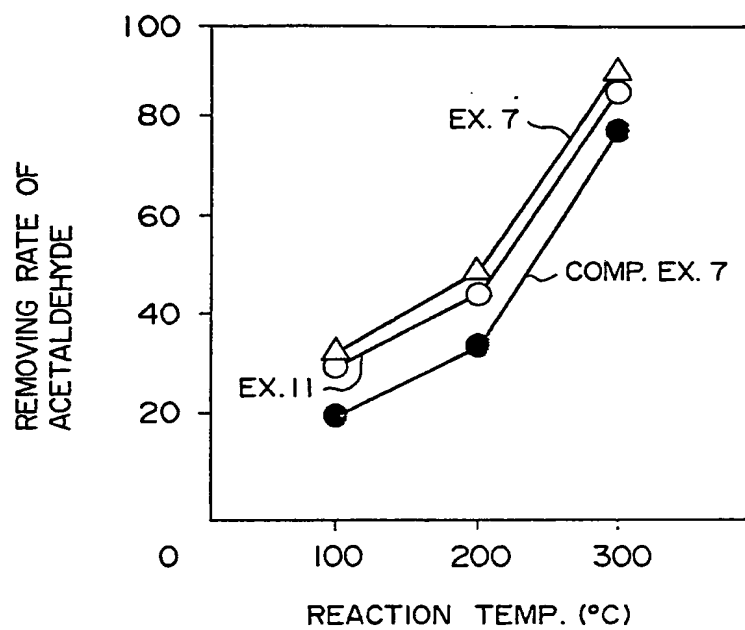


FIG. 11

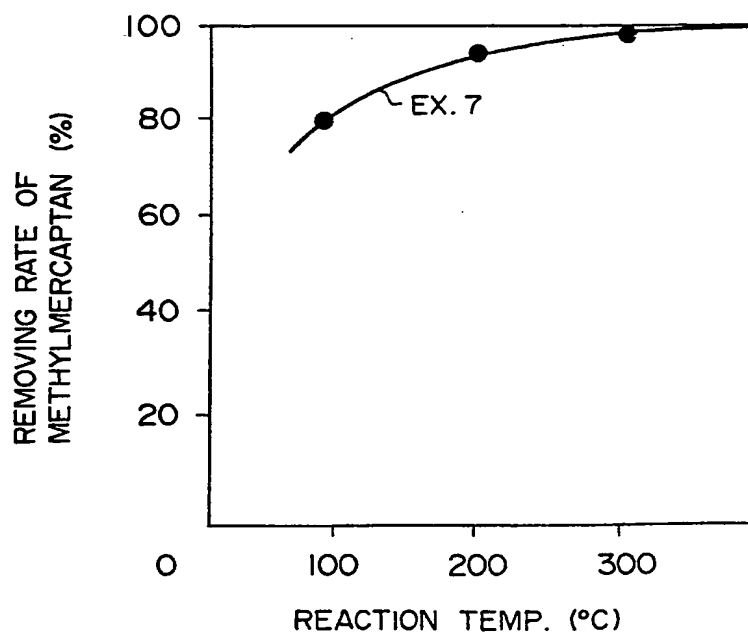


FIG. 12

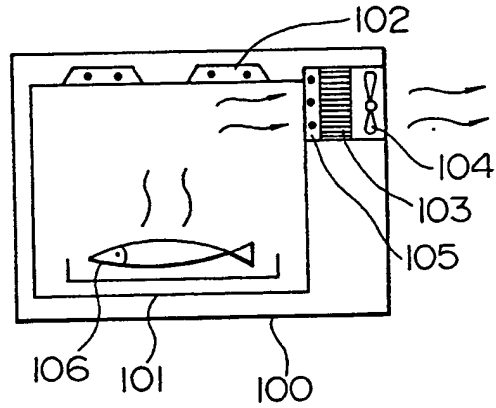


FIG. 13-1

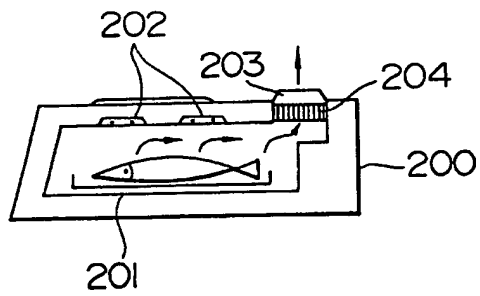


FIG. 13-2

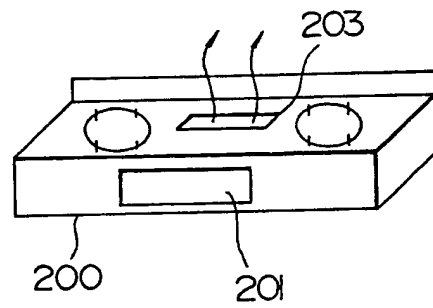
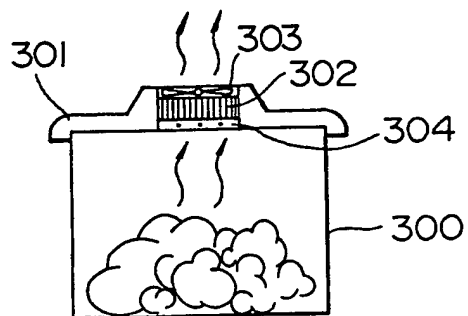


FIG. 14



CATALYST FOR OXIDATION OR DECOMPOSITION
OF GAS CONTAINING ODOR COMPONENTS

The present invention relates to an oxidation
or decomposition catalyst containing a novel active
5 component and in particular to a catalyst for oxidation
or decomposition of industrial off-gases and gases
containing odor components harmful and unpleasant to
human beings and natural environments which are generated
from household appliances and housing facilities at a
10 low temperature region between room temperature and
300°C.

For these last ten years there have been
continuously raised objections and problems on life
15 environments such as traffic noises and atmospheric
pollution and pollution of rivers caused by gases harmful
to human bodies and disagreeable odor gases which are
exhausted from factories. Techniques of catalytic
combustion of industrial gases or gases discharged from
20 automobiles on catalysts to make them harmless have been
employed from the 1970's and noble metals such as Pt,
Pd, and Rh have been generally used as active components
of the catalyst. Such catalytic combustion method is
further applied to various combustors and heaters as

1 clean combustion method generating no NOx and noble
metals are also generally used as active components of
the catalyst. However, noble metal catalysts are
expensive. Oxide catalysts which are inexpensive and
5 high in performance have been desired. For answering
such a demand, there have been proposed binary oxide
catalysts comprising silver oxide and manganese oxide
for catalytic combustion of hydrogen (Japanese Patent
Kokai No. 55-88850) and ternary oxide catalysts comprising
10 oxides of silver, cobalt and manganese for catalytic
combustion of carbon monoxide and hydrocarbons (Japanese
Patent Kokai No. 55-88855).

Recently, especially, need for removal of
gases harmful to human body and disagreeable odor gases
15 which are generated in room increases with more strict
regulation on exhaust gases and with changing life
style calling for more comfortable life circumstances.
Sources of harmful gases and disagreeable odor gases in
room include household combustors such as heaters, cooking
20 utensils, kitchen utensils, raw garbages, lavatory, etc.
Gases discharged from such household devices contain
not only carbon monoxide and hydrocarbons which are un-
combusted fuel components, but also various odor and
harmful components such as aldehydes, amines, alcohols,
25 and mercaptans. These gases are at low temperatures
from room temperature to about 300°C. Therefore, desir-
able catalysts for disposal of off-gases have been those
which have a high activity at a low temperature and are

1 low in production cost. However, the above-mentioned known
catalysts are directed to catalytic combustion of hydrogen,
carbon monoxide and hydrocarbons and are insufficient
for treatments of off-gases containing many of the above
5 odor components other than hydrogen, carbon monoxide and
hydrocarbons.

An object of the present invention is to provide
10 a catalyst for oxidation or decomposition of odor gases,
especially off-gases containing various kinds of harmful
and odor components which are generated in rooms.

Another object of the present invention is to
provide a catalyst for oxidation or decomposition which
15 exhibits a high activity at a low temperature of room
temperature to 300°C in oxidation and decomposition of
off-gases containing odor components which are generated
in households.

20 The oxidation or decomposition catalyst of the
present invention is a catalyst for oxidizing or decompos-
ing a gas containing odor components in the presence of
oxygen to make it harmless, which is characterized in that
it comprises a carrier and an active component supported
25 on the carrier; the active component contains silver
and manganese in an atomic ratio of silver to manganese

1 of 5:95 to 50:50; the silver is present in the form of
at least one of a compound with oxygen and a compound
with oxygen and manganese; manganese is present in
the form of at least one of a compound with oxygen and
5 compound with oxygen and silver; and the manganese oxide
contains manganese atoms having an oxidation number of
less than +4.

Suitable carriers for the oxidation or decomposition catalyst are porous carriers having a specific
10 surface area of $0.5 \text{ m}^2/\text{g}$ or more such as γ -alumina, TiO_2 ,
zeolite, silica and cordierite, because the supported active
components agglomerates if the specific surface area of the
carrier is smaller. Upper limit of the specific surface
area is preferably $1000 \text{ m}^2/\text{g}$. Especially a suitable
15 range is $50\text{-}1000 \text{ m}^2/\text{g}$.

The above catalyst may also be used as a
catalyst body comprising a substrate of ceramics or metal
and the catalyst coated thereon. The substrate may be
a honeycomb substrate, a plate-like substrate and a
20 metal gauze.

The present invention will be explained in
detail below.

The catalyst of the present invention is
obtained by adding an aqueous solution of a neutralizing
25 agent such as ammonia, an alkali carbonate, or an alkali
hydroxide to a mixed aqueous solution of silver nitrate
and water-soluble manganese salts such as manganese
nitrate, drying the resulting coprecipitate and then

1 oxidizing it with heating or separately producing
precipitates of silver and manganese by the above process,
kneading them, drying the mixture and then oxidizing
the mixture with heating. The catalyst can also be
5 produced by wet or dry mixing or kneading of a silver
salt such as silver oxalate, silver carbonate or silver
nitrate or silver oxide with a manganese salt such as
manganese acetate, manganese oxalate or manganese nitrate
or manganese oxide and then heat decomposing the
10 mixture.

The resulting catalyst is finally subjected to
heat treatment at 200-900°C, preferably 300-600°C in
the presence of an oxygen-containing gas.

The catalyst of the present invention can
15 contain, as an active component, at least one of iron,
cobalt, nickel, copper, vanadium, and zinc, and noble
metals of Group VIII of the periodic table such as
platinum and palladium in addition to silver and manganese
elements. Content of the elements other than silver
20 and manganese is preferably 1-10% by atom. For example, if
cobalt is contained in an amount of more than 10% by atom,
 AgCoO_2 is produced in a crystallized state to reduce
the activity of catalyst. If it is contained in an
amount of less than 1% by atom, effect of addition is
25 insufficient.

Mainly, Co is present in the form of CoO or
 Co_3O_4 , Fe is present in the form of Fe_2O_3 , Ni is present
in the form of NiO, Cu is present in the form of CuO or

1 Cu_2O , V is present in the form of V_2O_5 , Zn is present in the form of ZnO , Pd is present in the form of PdO or Pd, and Pt is present in the form of Pt.

Silver element of the thus produced Ag/Mn
5 binary catalyst forms a compound with oxygen or with oxygen and manganese element. That is, silver is not precipitated in a metallic form, but is in an oxidation state in the sense of an electron state. Usually, in the case of silver single component catalyst, Ag_2O
10 releases oxygen at higher than about 350°C and is precipitated as Ag at $300\text{--}600^\circ\text{C}$ which is a preferable heat treating temperature for the present invention. However, in the catalyst of the present invention, manganese oxide is present in the state of oxide of
15 manganese atom lower in oxidation number than the normally stable oxidation number of manganese atom in MnO_2 , namely, in the state of lower than +4 in oxidation number of manganese atom, thereby to keep silver in an oxidation state. As a result, the catalyst becomes highly active to the
20 oxidation reaction and, besides, silver is highly dispersed in the catalyst and agglomeration of particles can be suppressed.

Forms of compounds of silver and manganese elements of the catalyst can be identified by powder X-ray
25 diffraction (XRD), and the electron state (oxidization number) can be identified by an ordinary method such as X-ray photoelectron spectroscopy (XPS).

The catalyst of the present invention which

1 is mainly composed of silver and manganese can be used
as it is, but preferably supported on porous carriers
such as alumina, titania, and zeolite; ceramics carriers
such as cordierite; and metallic carriers such as
5 stainless steel, whereby the catalyst activity can be
sufficiently obtained. Furthermore, the catalyst
supported on the above carrier can further be supported
on a substrate such as ceramics or a metal by coating,
etc.

10 These catalysts can be prepared, for example,
by the following process: The precipitate containing
silver and manganese which is obtained by the afore-
mentioned process or oxides obtained by heat treatment
thereof or salts of silver and manganese are mixed and
15 kneaded with a carrier such as alumina or titania, or
a precursor sol thereof and then the mixture is heat
treated or the mixture is coated on a ceramic carrier
such as alumina or titania or a metallic carrier and
then, heat treated. Alternatively, a mixed aqueous
20 solution of a water-soluble silver salt and manganese
salt is impregnated in or coated on a ceramic carrier
or a metallic carrier and then dried and heat treated
to precipitate a catalyst mainly composed of silver and
manganese.

25 The shape of catalyst prepared by the above
process may be pellets molded from the powders, honeycomb,
sheet, plate, three-dimensional foam, etc.

 The catalyst of the present invention comprises

1 mainly silver and manganese and contains silver in the
form of a silver oxide and/or an oxide of silver and
manganese, and manganese in the form of a manganese
oxide and/or an oxide of manganese and silver, and
5 furthermore the manganese oxide contains a manganese atom
of oxidation number of less than +4. The manganese oxide
is present mainly in the form of Mn_2O_3 and/or Mn_3O_4 .
Part of silver in the catalyst forms a double oxide
with manganese. The form of the double oxide depends
10 on heat treating temperature and includes forms of
 $AgMn_2O_4$, $AgMnO_2$, $AgMnO_4$, $AgMnO$, Ag_2MnO_2 , or $Ag_2Mn_8O_{16}$
or a mixture thereof. The double oxide is most prefer-
ably in the form of $AgMn_2O_4$ or $AgMnO_2$.

The catalyst shows high activity for the
15 following reasons: That is, the oxidation state of silver
can be maintained by forming a double oxide of silver and
manganese; silver is highly dispersed to suppress its
agglomeration; and the double oxide is mixed with
manganese oxide resulting in high dispersion of silver.
20 The oxidation state of silver is maintained by keeping
the manganese atom of manganese oxide in an oxidation
state of less than +4 in oxidation number. The growth
of crystal of double oxide of silver and manganese is
also suppressed by mixing the double oxide with manganese
25 oxide.

All of the silver in the catalyst may not be
in the form of compound, but part of silver may be present
in the form of silver (metallic state) because silver is

1 mixed with manganese oxide and thus it is thermally
stable and highly active than in a single state.

The catalyst of the present invention is
especially effective for deodorizing harmful and
5 disagreeable odor gases of low concentration containing
various components which are generated by cooking foods
in an oven, grill or electronic oven.

When the catalyst of the present invention is
employed for these purposes, it is preferred to provide
10 it at the place inside the oven, grill or electronic oven
where the gas containing odor components generated by
cooking is dominant, that is, the place giving no
obstacles to the cooking, for example, the gas exhaust
passage, the inlet or outlet of the gas.

15 The catalyst of the present invention effec-
tively works at room temperature or higher, preferably
100-300°C. Temperature of disagreeable odor gases may
be at a lower temperature, depending upon cooking
conditions. In such case, it is desirable to keep the
20 catalyst in the temperature range which the catalyst
works effectively by providing a heater or the like
to make the catalyst work effectively.

The catalyst of the present invention can be
applied to cooking utensils such as an oven, a gas oven,
25 electronic oven and a gas table; apparatuses for disposal
of industrial wastes such as refuse incinerator and wet
refuse deodorizer, vehicles for carrying men or cargoes,
such as automobiles, electric tram cars, and airplanes;

1 toilet; and exhaust gas purification apparatuses for automobiles.

When the catalyst is applied to the oven, gas oven or electronic oven, the present catalyst is preferably
5 provided in the form of a layer in passages for discharging a gas from the grill. The gas in the grill is discharged through the catalyst layer by natural convention or by suction with an exhaust fan. The catalyst layer is desirably kept at a temperature within a range of
10 room temperature to 300°C. For heating the catalyst layer, it is preferred to provide a heater for heating the catalyst layer at a position before the catalyst layer in the passage for discharging the gas from the grill.

When the catalyst is applied to a gas table,
15 it is desired to provide a catalyst layer at a position before an exhaust vent for discharging smoke. The catalyst layer is preferably kept at a temperature within a range of room temperature to 300°C. This temperature range is kept preferably by adjusting the distance from
20 the grill heater to the catalyst layer.

When the catalyst is applied to apparatuses for disposal of industrial wastes such as refuse incinerator, the catalyst layer is preferably provided at the position in the passage up to a chimney for the smoke
25 generated in the refuse incinerator and containing odor components. The catalyst layer is kept at a temperature within a range of room temperature to 300°C.

When the catalyst is applied to a wet refuse

1 deodorizer, an exhaust vent for discharging the gas
generated from wet refuse and containing odor components
is provided at a deodorizing container and the catalyst
is preferably provided in the form of a layer in the
5 exhaust vent. It is desired to provide a heater for
heating the catalyst layer in the exhaust vent to keep
the catalyst temperature within a range of room
temperature to 300°C. It is also desired to provide a
fan at a position after the catalyst layer in the
10 exhaust vent.

When the catalyst is applied to vehicles for
carrying men or cargos such as automobiles, electric
tram cars and airplanes, the catalyst is preferably
provided in the form of a layer near the position where
15 the gas containing odor components are generated in
the vehicles. For example, it is desired to provide a
container having the catalyst layer and a fan which
sucks the gas containing odor components near the position
where men or cargoes are present.

20 When the catalyst is applied to toilets, the
catalyst is preferably provided in the form of a layer
in an exhaust vent for toilets. In order to keep the
catalyst layer at a temperature of room temperature
to 300°C, it is preferred to provide a heater for heating
25 the catalyst layer.

The catalyst layer is desirably of cartridge
type in order that it can be replaced with a new one

1 when its activity is deteriorated. Specifically,
a carrier on which catalyst active components are supported
is provided on a honeycomb-like or mesh-like substrate
by coating or other means and when it becomes necessary
5 to exchange the catalyst layer, the cartridge containing the
catalyst layer can be exchanged as it is. The substrate
can be made of a metal or ceramics such as cordierite.

The present catalyst can be used by contacting
a gas containing odor components with the catalyst in
10 the presence of oxygen at a temperature of room temperature
to 300°C.

The present invention will now be described in greater detail
by way of examples with reference to the accompanying drawings, wherein:-

Fig. 1 is a graph which shows relations between
15 the acetaldehyde removing rate and the content of silver
in active components when acetaldehyde was subjected
to a catalytic combustion using the catalyst prepared
in Example 1 and the catalyst prepared in Comparative
Example 1.

20 Fig. 2 is a graph which shows relations between
the acetaldehyde removing rate and the content of
silver in active components when acetaldehyde was sub-
jected to a catalytic combustion using the catalysts
prepared in Examples. 3, 4, and 5 and Comparative
25 Example 1.

Figs. 3-7 show X-ray diffraction patterns of
the catalysts prepared in the examples of the present
invention and comparative examples.

1 Fig. 8 is a graph which shows acetaldehyde
removing rate and trimethylamine removing rates
at various temperatures using the catalysts prepared
in Examples 6, 7, and 8 and Comparative Examples 4, 5
5 and 6.

Fig. 9 shows an X-ray diffraction pattern of
the catalyst prepared in Example 9.

Fig. 10 is a graph which shows relations between
the acetaldehyde removing rate and the reaction temperature
10 when acetaldehyde was subjected to a catalytic combustion
using the catalysts prepared in Examples 7 and 11 and
Comparative Example 7.

Fig. 11 is a graph which shows relations be-
tween the methylmercaptan removing rate and the reaction
15 temperature when methylmercaptan was subjected to a
catalytic combustion using the catalyst prepared in
Example 7.

Fig. 12 is a rough sketch of an oven provided
with the catalyst of the present invention.

20 Fig. 13-1 is a rough sketch of the side view
of a gas table provided with the catalyst of the present
invention.

Fig. 13-2 is a rough sketch of oblique view
of the gas table of Fig. 13-1.

25 Fig. 14 is a rough sketch of a wet refuse
deodorizer provided with the catalyst of the present
invention.

1 Preferred Embodiments of the Invention

The following nonlimiting examples will further explain the present invention in detail.

Example 1

5 2.276 g of silver nitrate and 40.436 g of manganese nitrate hexahydrate were dissolved in distilled water to make 300 cc of a solution. This mixed aqueous solution was uniformly absorbed in 500 g of γ -alumina powder (2-4 mm in diameter in spherical shape). Then, 10 the powder was dried at 120°C and heat treated at 500°C for 2 hours in air atmosphere to prepare an Ag/Mn catalyst supported on γ -alumina. Compositional ratio of Ag/Mn in the active components was Ag:Mn=10:90 (content of silver: 10% by atom) and the amount of active components 15 supported was 2 wt% based on the carrier after the heat treatment at 500°C. In the same manner, Ag/Mn catalysts supported on γ -alumina having ratios Ag/Mn (atomic ratio) of Ag:Mn=20:80, 30:70, 40:60, 50:50, and 70:30 were prepared. Furthermore, a catalyst of 100% Mn and 20 100% Ag supported on γ -alumina was also prepared in the same manner as above. Fig. 1 shows relations between reaction rate of odor component acetaldehyde and content of silver in the catalyst at reaction temperatures 200°C and 250°C. In the range of 50% by atom or less in content 25 of silver, effect of silver and manganese as a double oxide was exhibited and addition of silver in a small amount resulted in an increase of activity of a manganese

1 single component catalyst.

Example 2

8.4935 g of silver nitrate and 129.168 g of manganese nitrate hexahydrate were dissolved in distilled water to make 1500 cc of a solution. To this mixed aqueous solution was added dropwise aqueous ammonia obtained by diluting concentrated aqueous ammonia with distilled water twice in volume with stirring until pH reached 9. The produced precipitate was washed by decantation, then subjected to suction filtration and dried at 120°C. This was fired at 500°C for 2 hours. The powder was press molded and classified into 10-20 meshes to obtain an Ag/Mn catalyst. This catalyst had an atomic ratio of Ag:Mn=10:90.

15 Example 3

Example 2 was repeated except that 16.987 g of silver nitrate and 114.816 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having a compositional ratio (atomic ratio) of Ag:Mn=20:80.

Example 4

Example 2 was repeated except that 25.4805 g of silver nitrate and 100.464 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having an atomic ratio of Ag:Mg=30:70.

1 Example 5

Example 2 was repeated except that 33.974 g of silver nitrate and 114.816 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst
5 having an atomic ratio of Ag:Mn=50:50.

Comparative Example 1

Example 2 was repeated except that silver nitrate was not used and 143.52 g of manganese nitrate hexahydrate was used, thereby to obtain a manganese
10 oxide single component catalyst.

Comparative Example 2

85 g of silver nitrate was fired at 500°C for 2 hours and the resulting powder was ground and then press molded and classified into 10-20 mesh to obtain
15 an Ag single component catalyst.

The catalyst of the above Examples 1-5 is provided, for example, in the exhaust vent of an oven, a gas oven, an electronic oven or the like and is used as a deodorizing catalyst for a gas containing odor
20 components. An example where the catalyst of the present invention is provided in an oven is shown in Fig. 12 and an example where the catalyst of the present invention is provided in a gas table is shown in Figs. 13-1 and 13-2. In Fig. 12, reference numeral 100 indicates
25 an oven body, 101 indicates a grill, and 102 indicates a heater for the grill. The numeral 103 indicates a

1 catalyst provided in an exhaust vent, 104 indicates an
exhaust fan, and 105 indicates a heater for heating
the catalyst. The numeral 106 indicates food to be
cooked, which is a fish here. Structurally, the same can
5 be applied to the cases where the catalyst is applied
to a gas oven and an electronic oven.

In Fig. 13-1 and Fig. 13-2, 200 indicates a
gas table body, 201 indicates a grill for grilling food
such as a fish, 202 indicates a heater for grill, 203
10 indicates an exhaust vent for a gas containing odor
components generated by heating the food to be cooked,
and 204 indicates a catalyst layer provided in the exhaust
vent.

In these cooking utensils, acetaldehyde is
15 generated as an odor component in cooking.

Reaction rate of odor component acetaldehyde
was measured when the catalysts prepared in Examples 3,
4 and 5 and Comparative Example 1 were used. Fig. 2 shows
relations between the reaction rate at reaction tempera-
20 tures of 100°C and 125°C and the content of silver. As in
Fig. 1, use of the catalysts of Examples 3, 4 and 5
resulted in much increase of activity at a silver content
of 50% by atom or less as compared with use of the manganese
single component catalyst of Comparative Example 1 and
25 showed maximum activity at a silver content of 10% by atom.

Comparative Example 3

Example 2 was repeated except that 67.948 g

1 of silver nitrate and 57.408 g of manganese nitrate
hexahydrate were used, thereby to obtain an Ag/Mn
catalyst having an atomic ratio Ag:Mn=67.33.

Figs. 3-7 show powder X-ray diffraction patterns
5 of the catalysts prepared in Comparative Examples 1, 2
and 3 and Examples 2 and 4. Fig. 3, Fig. 4, Fig. 5,
Fig. 6 and Fig. 7 show diffraction pattern of the catalysts
of Comparative Example 1, Comparative Example 2, Compara-
tive Example 3, Example 2 and Example 4, respectively.

10 The manganese single component catalyst of Comparative
Example 1 is in the form of crystal of Mn_2O_3 and the silver
single component catalyst of Comparative Example 2 is
in the form of crystal of Ag (metallic state). On the
other hand, peak of Mn_3O_4 and peak of a part of Ag_2O were
15 recognized in XRD pattern of Example 2. The Ag/Mn catalyst
had a crystal form different from that of single component
catalyst due to its double oxide effect. In order to know
more detailed state of oxidation number, bound energy of
silver atom and manganese atom was measured by X-ray
20 photoelectron spectroscopy. The manganese atom in the
catalyst of Example 2 was in a somewhat lower energy state
than Mn_2O_3 and the catalyst totally is in the state of
lower than +3 in oxidation number. Silver atom can be
said to have an oxidation number of +1 because it is
25 in the same energy state as Ag_2O . However, it was also
presumed that silver atom formed a double oxide with
manganese because the peak intensity of Ag_2O was weak in
XRD pattern of Fig. 6. Peaks of Mn_3O_4 and $AgMn_2O_4$

1 were recognized in XRD pattern of example 4 of Fig. 7
and presence of double oxide which was foreseen in
Example 2 was confirmed. According to XRD pattern of
Comparative Example 3 shown in Fig. 5, in the composition
5 of high silver content which showed no double oxide effect
in the results of Example 1 of Fig. 1, the silver was
precipitated in metallic state and it can be said from
the results that one of the factors for high activation
is that silver is in an oxidation state.

10 Example 6

29.3 g of silver nitrate and 97.6 g of
manganese nitrate hexahydrate were dissolved in distilled
water to obtain 400 cc of a mixed aqueous solution.
γ-alumina honeycomb having a specific surface area of
15 $150 \text{ m}^2/\text{g}$ and having 100 cells/inch^2 was dipped in the
above mixed aqueous solution for 2 minutes, then dried
at 120°C and thereafter, heat treated at 500°C for 1
hour in air atmosphere. This procedure was repeated
twice to obtain a final catalyst. This catalyst had an
20 atomic ratio Ag:Mn=30:70.

Example 7

A catalyst was prepared in the same manner
as in Example 6 except that 8.90 g of silver nitrate
and 134.4 g of manganese nitrate hexahydrate were used.
25 This catalyst had an atomic ratio Ag:Mn=10:90.

1 Example 8

5.31 g of silver nitrate, 80.4 g of manganese nitrate hexahydrate, 100 g of γ -alumina powder of 250 m²/g in specific surface area, and 40 cc of distilled water were kneaded for about 1 hour. The resulting slurry was dried at 120°C and then, fired at 500°C for 2 hours.

The resulting oxide was classified into 200 mesh or less and a binder and distilled water were added thereto to prepare a slurry. This slurry was coated on a cordierite honeycomb having 100 cells/inch² and this was dried at 120°C and fired at 500°C for 2 hours.

Comparative Example 4

A silver catalyst was prepared in the same manner as in Example 6 except that 79.41 g of silver nitrate was used and manganese nitrate hexahydrate was not used.

Comparative Example 5

A manganese oxide catalyst was prepared in the same manner as in Example 7 except that silver nitrate was not used and 183.27 g of manganese nitrate hexahydrate was used.

Comparative Example 6

Aqueous ammonia was added dropwise to a solution prepared by dissolving 48.2 g of silver nitrate in 1 liter of distilled water and the resulting sol was

1 filtered and dried and then fired at 500°C for 2 hours
to obtain silver catalyst powder. Separately, aqueous
ammonia was added dropwise to a solution prepared by
dissolving 75.6 g of manganese nitrate hexahydrate in
5 1 liter of distilled water and the resulting sol was
filtered and dried and then, fired at 500°C for 2 hours
to obtain manganese oxide. The silver catalyst, the
manganese oxide and γ -alumina powder having a specific
surface area of 250 m²/g were mixed in a weight ratio
10 of 3:7:90 and wet kneaded. The mixture was dried and
press molded and classified to 40-68 meshes to obtain a
catalyst. Peaks of γ -alumina, Ag, and MnO₂ were seen
in X-ray diffraction pattern of this catalyst.

Removing rate was measured on the catalysts
15 of Examples 6, 7 and 8 and Comparative Examples 4, 5
and 6 at reaction temperatures of 100°C, 200°C and 300°C
under the conditions of SV: 30000 h⁻¹ and reaction gas:
60 ppm of acetaldehyde, 60 ppm of trimethylamine and air
as a base. The results are shown in Fig. 8.

20 The catalysts of examples 6, 7 and 8 were
higher in removing rate than those of Comparative Examples
4, 5 and 6 and especially were high in activity at
100-300°C. Therefore, the catalysts of Examples 6,
7 and 8 show effective catalyst activities even if the
25 temperature of disagreeable odor gas generated is low.
In the case of such system as heating the disagreeable
odor gas or catalyst by heater to keep a high reaction
temperature, the effect can be exhibited without causing

- 1 slipping of gas even at a low temperature during elevation of temperature by heater.

Example 9

25.48 g of silver nitrate and 43.06 g of
5 manganese nitrate hexahydrate were dissolved in 2
liters of distilled water to obtain a mixed aqueous
solution. Aqueous ammonia prepared by diluting
concentrated aqueous ammonia with distilled water twice
in volume was added dropwise to the above mixed aqueous
10 solution with stirring to produce a precipitate. This
precipitate was washed twice by decantation, then
subjected to suction filtration and dried at 120°C.
This was fired at 300°C for 2 hours to obtain a catalyst.

The catalyst was analyzed by powder X-ray
15 diffraction. The X-ray diffraction pattern thereof is
shown in Fig. 9. In Fig. 9, ∇ shows a peak peculiar
to Mn_2O_3 and \blacktriangledown shows a peak peculiar to $AgMn_2O_4$. There-
from it can be seen that the catalyst contained manganese
oxide and double oxide of silver and manganese.

20 Example 10

A coating slurry was prepared in the same manner
as in Example 9 except that 68.66 g of manganese acetate
tetrahydrate was used in place of manganese nitrate hexa-
hydrate. This was coated on a metal gauze of stainless
25 steel on which alumina had been flame sprayed and dried and
then fired at 500°C for 2 hours. Using a stack of 22

1 sheets of this metal gauze type catalyst, the removing rate
was measured at a reaction temperature of 250°C under
the conditions of SV: 30000 h⁻¹ and reaction gas: 50 ppm
of acetaldehyde, 50 ppm of trimethylamine and air as a
5 base. In this case, the removing rate of acetaldehyde was
80% and that of trimethylamine was 90%. Since this
metal gauze type catalyst had a higher thermal conductivity
than catalyst comprising only an oxide, the temperature of
the catalyst layer rapidly increased by the reaction gas
10 or the heater and this catalyst was also found to be
systemically effective.

Example 11

A catalyst was prepared in the same manner as
in Example 6 except that 8.90 g of silver nitrate,
15 134.4 g of manganese nitrate and 13.265 g of cobalt
nitrate were used. This catalyst had an atomic ratio
Ag:Mn=10:90 and atomic % of Co in total number of such
atoms Ag, Mn and Co was 8%.

Comparative Example 7

20 A catalyst was prepared in the same manner
as in Example 6 except that 8.90 g of silver nitrate,
134.4 g of manganese nitrate and 138.472 g of cobalt
nitrate were used. This catalyst had an atomic ratio
Ag:Mn=10:90 and atomic % of Co in total number of such
25 atoms as Ag, Mn and Co was 50%.

Under the same experimental conditions as in

1 obtaining the data of Fig. 10, the acetaldehyde removing
rate was measured for catalysts of Examples 7 and 11
and Comparative Example 7. The catalyst of Example 11
which corresponds to the catalyst of Example 7 to which
5 8% by atom of Co was added had substantially no difference
in activity from that of Example 7. However, the
catalyst of Comparative Example 7 which corresponds to
the catalyst of Example 7 to which Co atom was added
in an amount of 50% by atom was inferior in activity to
10 the catalyst of Example 7.

Using the catalyst of Example 7, removing
rates at reaction temperatures of 100, 200, and 300°C
were measured under the conditions of $SV=30000\text{ h}^{-1}$ and
reaction gas comprising 60 ppm of methyl mercaptan
15 (CH_3SH) and air as a base. The results are shown in
Fig. 11. Mercaptan was generated when meats or vegetables
decayed. An example of generation of such an odor compo-
nent is a wet refuse deodorizer. Fig. 14 shows an example
of a wet refuse deodorizer provided with the catalyst
20 of the present invention. An exhaust vent for dis-
charging gas generated from the wet refuse is provided
at cover 301 of deodorizer 300 and in this exhaust vent
are provided catalyst 302, a heater 304 for heating
catalyst layer 302 and a fan 303 for discharging the
25 gas deodorized by the catalyst layer 302. The results
of measurement of removing rate of mercaptan for applica-
tion of the catalyst to such use was that the removing

- 1 rate was 80% at a reaction temperature of 100°C and the catalyst showed a high activity at the low temperature.

CLAIMS:-

1. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.
2. A catalyst according to claim 1, wherein the carrier has a specific surface area of 0.5 to 1000 m²/g.
3. A catalyst according to claim 1, wherein the carrier is one member selected from the group consisting of γ -alumina, TiO₂, zeolite, silica and cordierite.
4. A catalyst according to claim 1, which contains at least one manganese oxide selected from the group consisting of Mn₂O₃ and Mn₃O₄.
5. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like

or metal gauze-like substrate comprising ceramics or metal, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

6. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having a oxidation number of less than +4, the active component being prepared by mixing at least one compound selected from the group consisting of a silver salt and silver oxide with at least one compound selected from

the group consisting of a manganese salt and manganese oxide and finally heat treating the mixture at 200 to 900°C in the presence of an oxygen-containing gas.

7. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like or metal gauze-like substrate comprising ceramics or metal, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4, the active component being prepared by mixing at least one compound selected from the group consisting of a silver salt and silver oxide with at least one compound selected from the group consisting of a manganese salt and manganese oxide and finally heat treating the mixture at 200 to 900°C in the presence of air.

8. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises

a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt, nickel, copper, vanadium, zinc and noble metals of Group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and contains the noble metal as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

9. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like or metal gauze-like substrate, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt,

nickel, copper, vanadium, zinc and noble metals of Group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and contains iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and the noble metal of Group VIII of the periodic table as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

10. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which contains, as an active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

11. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which contains,

as an active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt, nickel, copper, vanadium, zinc and noble metals of group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and contains iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and the noble metal of Group VIII of the periodic table as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

12. A catalyst for oxidation or decomposition of a gas containing odor components at a temperature of from room temperature to 300°C in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a

compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

13. A cooking utensil, which comprises a grill for cooking a food by heating, a heater for the grill and an exhaust vent for discharging a gas containing odor components generated in the grill, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

14. A cooking utensil according to claim 13, which is an oven, a gas oven, an electronic oven or a gas table.

15. An industrial waste disposal equipment, which comprises an incinerator for incinerating industrial wastes and an exhausting means for an off-gas containing odor components generated in the incinerator, the exhausting means being provided with a catalyst layer which comprises a carrier and an active component supported

on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

16. A wet refuse deodorizer, which comprises a container for containing wet refuses provided with an exhaust vent for gas generated in the container, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

17. A vehicle for carrying men or cargoes, which comprises a catalyst layer provided near a position where men or cargoes are present, the catalyst layer which comprises

a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4, and an exhausting means for discharging gas deodorized by the catalyst layer.

18. A toilet, which comprises a toilet stool and an exhaust vent for discharging gas containing odor components generated by use of the toilet stool, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4 and a heater for

heating the catalyst layer to a temperature of from room temperature to 300°C provided at a position before the catalyst layer in the exhaust vent.

19. A cartridge type deodorizing catalyst which comprises a carrier and an active component supported on the carrier which are provided on a substrate and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

20. A method for use of a catalyst which comprises contacting a gas containing odor components with a catalyst which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a

manganese atom having an oxidation number of less than +4 in the presence of oxygen at a temperature of from room temperature to 300°C, thereby oxidizing or decomposing the gas containing odor components.

21. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen substantially as herein described with reference to the accompanying drawings.